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Effect of the Z- and macro-R-group on the thermal desulfurization of polymers synthesized with acid/base "switchable" dithiocarbamate RAFT agents[a]

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Thermolysis has been examined as a method for complete desulfurization of RAFT-synthesized polymers prepared with acid/base "switchable" *N*-methyl-*N*-pyridyldithiocarbamates [R-S_2CZ or R-S_2CZH$^+$]. The low molar mass macro-RAFT agents derived from more activated monomers (MAMs) (i.e., styrene (St), *N*-isopropylacrylamide (NIPAm) and methyl methacrylate (MMA)) with R-S_2CZH$^+$ and less activated monomers (LAMs) (i.e., vinyl acetate (VAc) and *N*-vinylpyrolidone (NVP)) with R-S_2CZ were prepared by RAFT polymerization and analyzed by thermogravimetric analysis. In all cases, a mass loss consistent with loss of the end-group (Z-CS_2H) could be observed at a temperature lower than, and largely discrete from, that required for further degradation of the polymer, thereby indicating that thermolysis was a potentially viable method for thiocarbonylthio end-group removal. The onset temperature for end-group loss and, in some cases, the new end-groups formed were strongly dependent on the identity of the R-$(P)_n$ and the charge state of the pyridyl Z group of the macro-RAFT agent; increasing in the series poly(MMA)< poly(St)~ poly(NIPAm)<< poly(VAc)~ poly(NVP) for -S_2CZ (i.e., end-group neutalized before

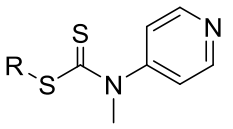
[a] **Supporting Information** is available online from the Wiley Online Library or from the author.

thermolysis for poly(MAMs)) and poly(MMA)< poly(St)~ poly(NIPAm) for $-S_2CZH^+$. Small scale preparative experiments were conducted to provide a preliminary asessment of thermolysis as a means of end-group removal. Clean end-group removal is shown possible for poly(St) and poly(NVP). For poly(NIPAm) the thiocarbonyl chain end is removed, but the end-group identity is less certain. For poly(MMA) and poly(VAc) some degradation of the polymer accompanied end-group loss under the conditions used and further refinement of the process is required.

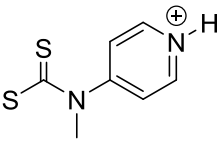
1. Introduction

Reversible addition-fragmentation chain transfer (RAFT) polymerization[1] has many advantages over other techniques for reversible deactivation radical polymerization (RDRP),[2] arguably the most significant of these being the method's applicability to a greater variety of monomers.[3-8] Historically, it has sometimes been a challenge to select the RAFT agent for the monomer(s) being polymerized, specifically in cases where polymerization involved monomers of disparate activity. However, several approaches to tailoring the structure and thereby the activity of thiocarbonylthio RAFT agents to suit the reactivity of the monomers and propagating species have been described.[9]

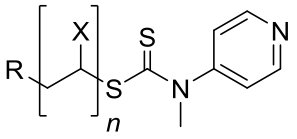
A prime example are acid/base switchable *N*-pyridyl-functional dithiocarbamate RAFT agents,[10-16] which provide the ability to control the polymerization of both more activated monomers (MAMs) and less activated monomers (LAMs). By switching the RAFT agent Z-group between a neutral pyridyl (e.g., in **1** or **2**) and a charged pyridinium moiety, (e.g., in **1**-H^+ or **2**-H^+) low dispersity block copolymers comprising both MAMs and LAMs can be prepared.



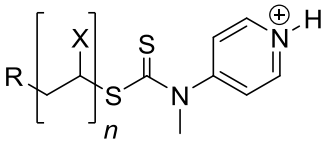
1 (R=CH_2CN)
2 (R=$C(CH_3)_2CN$



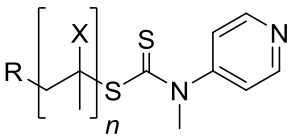
1-H$^+$(R=CH_2CN)
2-H$^+$(R=$C(CH_3)_2CN$



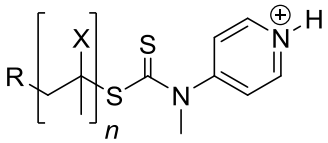
PSt-1(R=CH_2CN, X=Ph)
PNIPAm-1(R=CH_2CN, X=$CONHCH(CH_3)_2$)
PVAc-1(R=CH_2CN, X=$OCOCH_3$
PNVP-1(R=CH_2CN, X=2-pyrrolidone



PSt-1-H$^+$(R=CH_2CN, X=Ph)
PNIPAm-1-H$^+$(R=CH_2CN, X=$CONHCH(CH_3)_2$)



PMMA-2(R=$C(CH_3)_2CN$), X=$COOCH_3$)



PMMA-2-H$^+$(R=$C(CH_3)_2CN$), X=$COOCH_3$)

The thiocarbonylthio functionality of a RAFT agent (Z-C(=S)-S-R) delivers control over the polymerization and the Z-C(=S)-S- is retained as a functional handle for further polymer manipulation, which might involve another RAFT polymerization step, e.g., to form block, star or other architectures, or some form of end-group transformation.[17-18] However, for certain applications it may be desirable simply to remove this functionality post-polymerization. For example, dependent on the specific Z and R groups, the thiocarbonyl functionality may be reactive towards nucleophiles and/or prone to unwanted thermal or photochemical transformation.[18] Again dependent on the specific Z and R groups, certain RAFT-synthesized polymers are coloured (note that the present RAFT agents are only highly coloured in the switched, protonated state and can be decolourized by neutralization). RAFT-synthesized polymers may also develop odour on storage due to the formation of volatile sulfur compounds (the latter is notably less of an issue with dithiocarbamates). As a response to these concerns, various end-group removal techniques have been developed,[17-18] which include reaction with nucleophiles (e.g., aminolysis,[19-23] borohydride reduction),[24-25] radical-induced reactions (e.g., coupling,[26-27] reduction,[28-31] oxidation[32-33]) and thermolysis.[34-36] However, there are few studies on dithiocarbamate end-group removal[37-41] and none of these relate to the switchable RAFT agents.

In our previous investigations,[10, 12-14, 16] the *N*-pyridyl-functional dithiocarbamate RAFT agents and their derived polymers were found to be unusually robust. For example, their high hydrolytic stability allows aqueous polymerization in strongly acidic solution (e.g., $\leq$ pH 2) with no discernible loss of end-group functionality.[12] Attempted end-group removal via aminolysis was also ineffective.[42] These observations provided the motivation to develop an efficient method to remove the dithiocarbamate chain-ends.

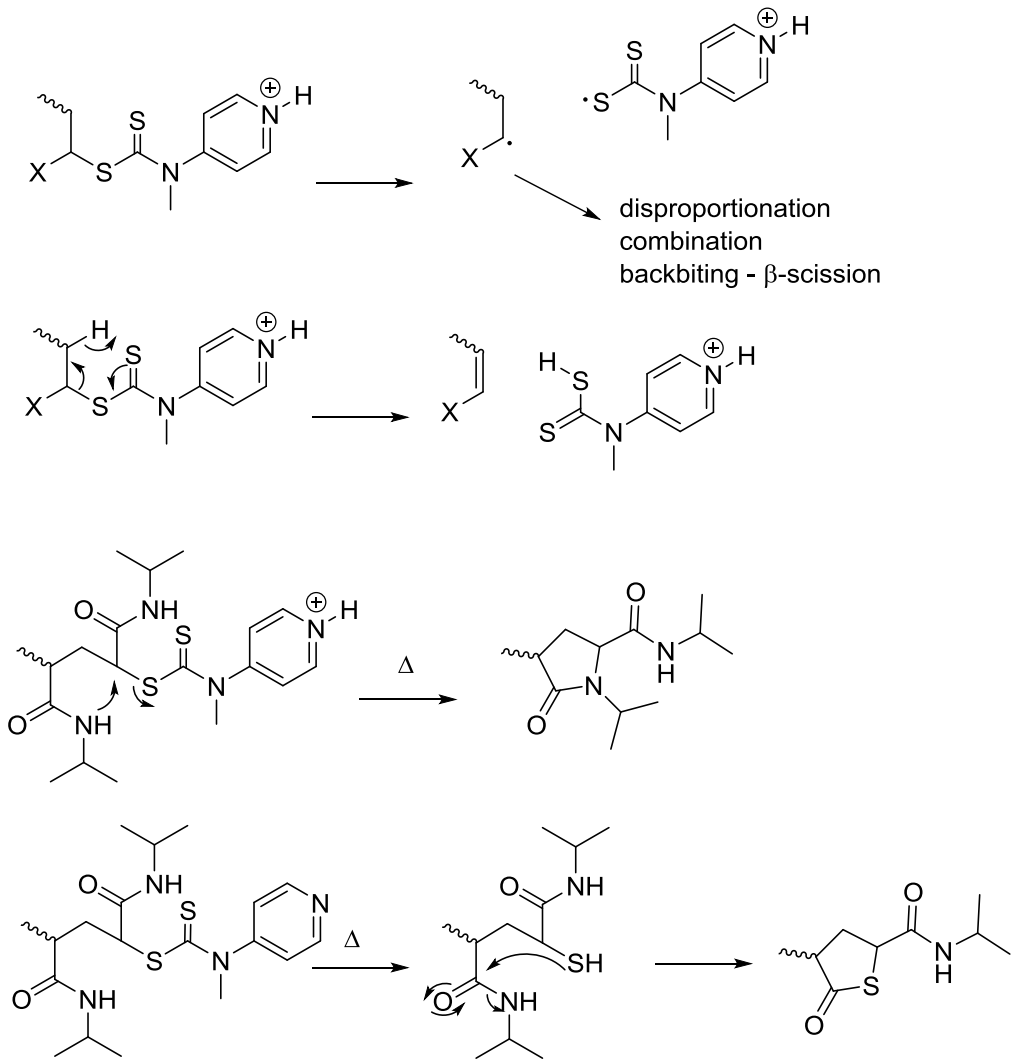
In contrast to most other techniques for thiocarbonylthio end-group removal, thermolysis can provide for desulfurization without a need for additional reagents. Thermolysis is operationally simple in that it is conducted by simply heating the polymer usually in the absence of oxygen. There are now many examples of thermogravimetric analysis (TGA) applied to RAFT-synthesized polymers to establish the conditions for end-group removal and to evaluate the effect of end-group on the decomposition of the polymer.[20, 35-36, 43] To date TGA has been used to study end-group loss for RAFT polymers synthesized with xanthates,[44] trithiocarbonates[34, 36] and dithiobenzoates.[21, 36, 44-45] Studies with model compounds for RAFT agents show that dithiocarbamates are more thermally stable than other RAFT agents, with *N*,*N*-dialkyldithiocarbamates being stable under condition where facile end-group elimination is seen for similar dithioesters, trithiocarbonate and xanthates.[46-49] PMMA with *N*,*N*-dialkyldithiocarbamate ends formed with a dithiuram disulfide as thermal iniferter was found to be stable to thermolysis with no mass loss at temperatures < 300 °C.[50]

With this background it was imperative to establish a convenient method for end-group removal for polymers prepared with "switchable" *N*-methyl-*N*-pyridyldithiocarbamates. Herein, we report on the thermolysis of a series of low molar mass polymers prepared with the RAFT agents and, with some constraints that will be described, propose thermolysis as a viable method in this context.

3. Results and Discussion

RAFT-synthesized polymers typically undergo thermal end-group decomposition by one of two main pathways: (a) concerted electrocyclic elimination (a Chugaev process)[36] or (b) C-S bond homolysis, to reform propagating radicals that can subsequently react by a variety of pathways that include, β-scission (e.g., PMMA unzipping), backbiting followed by β-scission (e.g., PSt, poly(*n*-butyl acrylate) unzipping), disproportionation or combination.[34, 36] The predominant pathway depends

strongly on the specific polymer, the RAFT end-group and the thermolysis conditions. Depending on the pendant functionality of the polymer other pathways may also contribute (see Scheme 1).



Scheme 1. Proposed mechanisms for end-group loss during thermolysis of macro-RAFT agents prepared with *N*-methyl-*N*-pyridyldithiocarbamates.

3.1. Synthesis of homopolymers

A series of polymers with low molar mass and low molar mass dispersity were prepared from MAMs (styrene (St), *N*-isopropylacrylamide (NIPAm), and methyl methacrylate (MMA)) and LAMs ((vinyl acetate (VAc) and *N*-vinylpyrrolidone (NVP)). Cyanomethyl *N*-methyl-*N*-(pyridin-4-yl)carbamodithioate **1** was used as RAFT agent to mediate polymerization of monosubsituted monomers. For MMA polymerization (a 1,1-

disbsituted monomer) it was necessary to use 2-cyanopropan-2-yl *N*-methyl-*N*-(pyridin-4-yl)carbamodithioate **2** as RAFT agent. The polymerization conditions are based on previous work: St,[10] NIPAm,[14] MMA,[19] VAc,[13] NVP[14] (see Table S1). For poly(LAM) the RAFT agent was used in its unswitched (neutral) form. For poly(MAM), the RAFT agent was used in its switched (protonated) form; achieved by addition of a stoichiometic amount of *p*-toluenesulfonic acid. To establish the affect of acid on thermolysis, a portion of the poly(MAM) was passed through a column of sodium carbonate to neutralize the pyridinium-functional Z-group prior to purification by precipitation.

3.2 Thermolysis of homopolymers

For thermogravimetric analysis, the polymers were heated at a ramp rate of 5 °C/min to a maximum of 500 °C (Figure 1). Higher ramp rates resulted in a thermogram with sigificantly decreased resolution. In all cases, a mass loss consistent with loss of Z-C(=S)SH was observed at a temperature lower than and largely discrete from that required for further degradation of the polymer (Table 1). Upon ascertaining temperatures required for thiocarbonylthio end-group loss, a preparative isothermal decomposition was performed above the temperature of end-group loss for subsequent analysis.[51] The extent of end-group removal for each polymer was assessed by ^{1}H NMR and by SEC analysis with UV detection at 306 nm, where the *N*-methyl-*N*-(pyridin-4-yl)carbamodithioate chromophore absorbs in the UV and there is little absorption by the chromophores present in the monomer units (see Figure 2 and S2 to S11 in the Supporting Information).[18] Quantitative removal of the thiocarbonylthio chromophore was confirmed in all cases (see Table 1).

Table 1: Thermolysis data from TGA analysis of polymers prepared with RAFT agents **1** or **2**.

Entry	Polymer	$M_{n\,(NMR)}$ (g mol^{-1})[a]	T (peak) (^{o}C)[b]	T (range) (^{o}C)[c]	End-group mass loss (calc.) [d] (%)	End-group mass loss (%)	residual mass @ 400 ^{o}C (%)
1A	PSt-**1**-H^{+}	6500	185	170-215	2.9	3.3	9[e]
1B	PSt-**1**		224	205-235		4.4	4[e]
2A	PNIPAm-**1**-H^{+}	2600	197	165-210	7.8	7.8	8[e]
2B	PNIPAm-**1**		232	210-240		8.1	5[e]
3A	PMMA-**2**-H^{+}	5000	121	110-135	4.2	4.8	12
3B	PMMA-**2**		136	120-150		4.3	13
4	PVAc-**1**	2700	293	285-325	2.2	2.5	7[e]
5	PNVP-**1**	9400	306	290-315	6.1	7	4[e]

[a] Calculated by end-group analysis via ^{1}H NMR of the protonated polymers for MAMs and neutral polymers for LAMs [b] peak temperature for end-group loss, obtained from the differential thermogravimetry (DTG) curve, [c] temperature range for end-group loss, obtained from the TGA curve, [d] based on the mass % loss of the product $C_7N_2S_2H_8$ (Z-C(=S)SH): % mass loss = [184.21]/[M_n Polymer] × 100 %, [e] no residual material was observed on the pan after thermolysis of these samples.

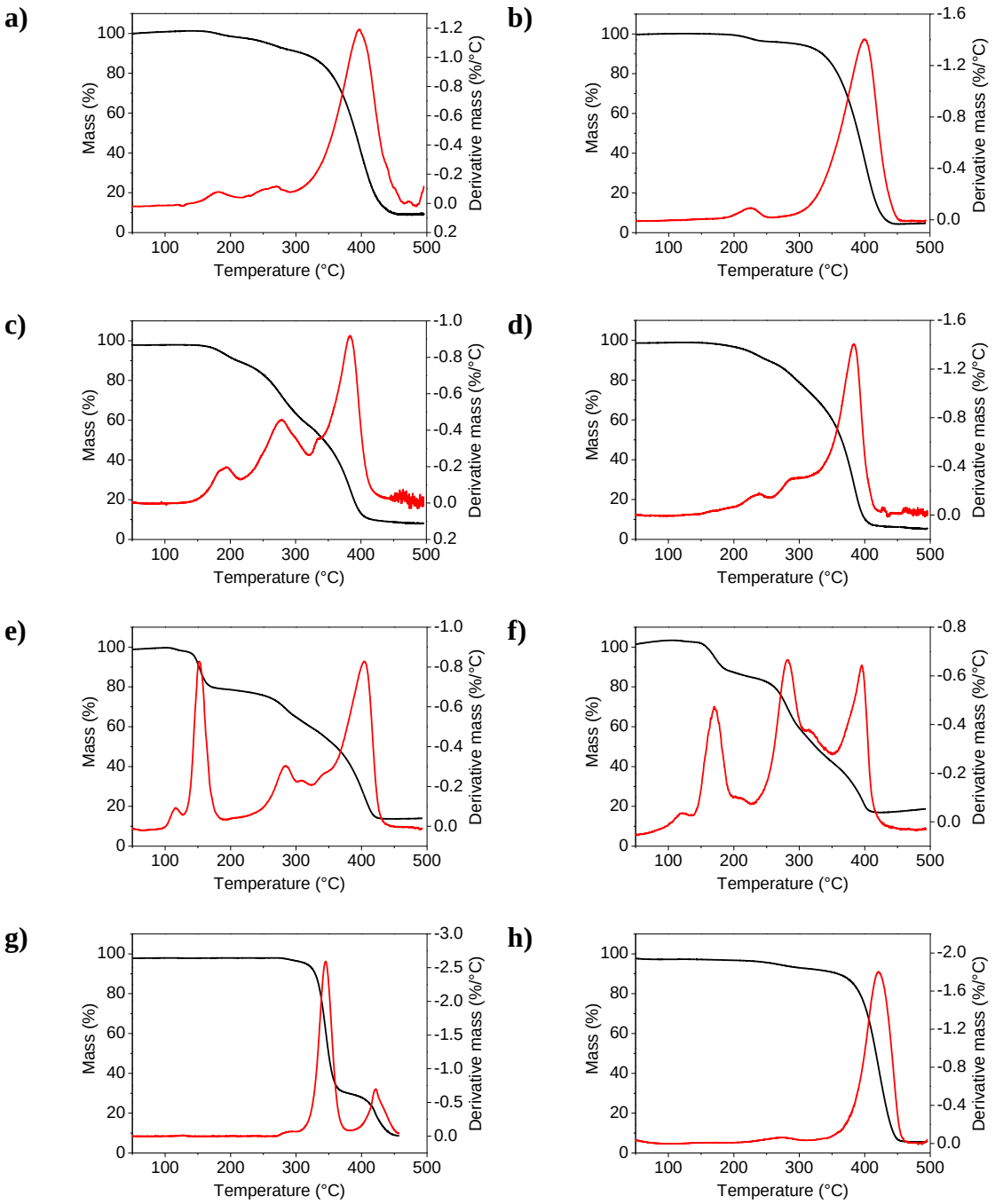


*Figure 1:*TGA (black) and first derivative (red) curves of a) PSt-**1**-H^+, b) PSt-**1**, c) PNIPAm-**1**-H^+, d) PNIPAm-**1**, e) PMMA-**2**-H^+, f) PMMA-**2**, g) PVAc-**1**, h) PNVP-**1**.

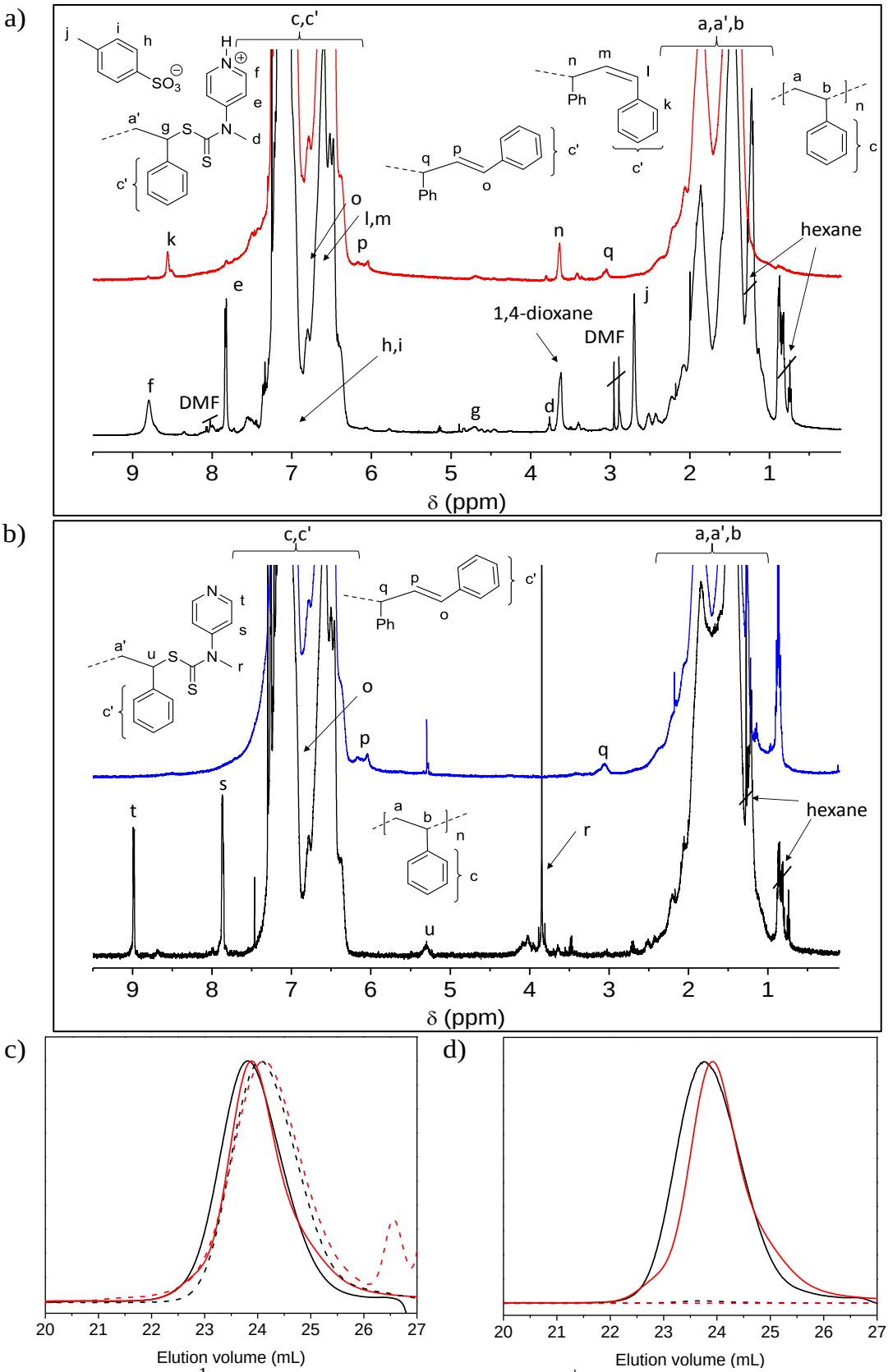


Figure 2: Expanded ^{1}H NMR spectra for (a) PSt-**1**-H^{+} as prepared (black lines), PSt-**1**-H^{+} after exposure to 210 °C for 2.5 h under vacuum (red lines), and (b) PSt-**1** as prepared (black lines) and PSt-**1** exposed to 240 °C for 2.5 h under vacuum (blue lines), and normalized SEC chromatograms with (c) differential refractive index detection and (d) UV detection at 306 nm (UV306) for PSt-**1**-H^{+} (black lines) and PSt-**1** (red lines), as prepared (solid lines) and following thermolysis (dashed lines).

3.3 Polymers from more activated monomers (MAMs)

3.3.1 Polystyrene

In the protonated form polystyrene (PSt-**1**-H^+) shows a mass loss corresponding to loss of the RAFT end-group within the temperature range 170-215 °C (Table 1, Entry 1A and Figure 1a). For the neutral form, PSt-**1**, the temperature required for end-group loss was higher with end-group loss occurring between 205-235 °C (Table 1, Entry 1B and Figure 1b).

^{1}H NMR analysis following preparative isothermal treatment confirmed complete end-group removal, evidenced by the loss of pyridyl resonances at approximately 8.9 and 7.8 ppm (see Figure 2a). End-group removal was also verified by SEC. Traces obtained with refractive index detection were essentially the same for the polymer before and after thermolysis (see Figure 2b). However, traces obtained with UV detection at 306 nm (where polystyrene is essentially transparent) are consistent with quantitative removal of the RAFT agent-derived chromophore (see Figure 2c).

Thermolysis of PSt-**1** gives PSt with a *trans*-1,3-diphenylpropene end (this is also observed with PSt trithiocarbonates).[34-35, 52] On the other hand, thermolysis of the protonated form, PSt-**1**-H^+, gives PSt with a mixture of *cis* and *trans*-1,3-diphenylpropene ends. This may indicate acid-catalyzed isomerization of the initially formed end. A second mass loss observed for PSt-**1**-H^+ over the temperature range 215-290 °C may correspond to loss of *p*-toluenesulfonic acid.[53]

Previously thermolyses of PSt prepared using trithiocabonate RAFT agents have been conducted. A PSt prepared with phthalimidomethyl butyl trithiocarbonate (M_n 1850)[34-35] was heated at 10 °C/min and showed an onset temperature for trithiocabonate end-group loss of 210 °C and complete loss between 200-270 °C.[54] Under similar conditions a PSt prepared with 1,4-bis-((phthalimidomethylsulfanylthiocarbonyl)sulfanyl)butane[55] (M_n 51100) showed an onset temperature for trithiocarbonate end-group loss of 200 °C and complete loss

between 200-250 °C. In each case a preparative experiment showed that the trithocarbonate functionality could be cleanly and quantiatively eliminated to provide a colourless product. The ^{1}H NMR indicated formation of PSt with a *trans*-1,3-diphenylpropene end.

3.3.2 Poly(*N*-isopropylacrylamide)

The protonated PNIPAm-**1**-H^{+} undergoes no appreciable change until 165 °C, when a mass loss corresponding to that expected for RAFT end-group occurs over the range 165-210 °C. Complete degradation of PNIPAm-**1**-H^{+} occurs by 400 °C (Figure 1c). The neutral PNIPAm-**1** displayed a different end-group mass loss over the range 210-240 °C, with a peak at much higher temperature (Figure 1d), while the final degradation also occurs at about 400 °C. The initial mass loss in each case was consistent with the loss of the RAFT-derived end-group only. SEC analysis of polymers derived from isothermal experiments indicate complete end-group loss (see Figure S2). The peaks in the ^{1}H NMR spectra that would be indicative the presence of a vinylic end-group were not observed in significant amounts for either the thermolyzed PNIPAm-**1**-H^{+} or PNIPAm-**1** (see Supporting Information, Figure S3).

There are few previous investigations of RAFT end-group removal from polyacrylamides, in particular. poly(NIPAm) or poly(*N*,*N*-dimethylacrylamide) with trithocarbonate[56] or dithiobenzoate ends.[52] In the latter case unsaturated chain ends were also not observed and the NMR spectrum of the product is similar to that seen for thermolyzed PNIPAm-**1**. A possibility is thiolactone formation, this end-group might expected if the initial product of end-group loss was a thiol chain end (Scheme 1). Thiol chain ends might arise by aminolysis if there was some amine was produced by decomposion of the amide side groups. End-groups formed by thermolysis of PNIPAm-**1**-H^{+} are different possibly because any amine formed is immediately

scavenged by acid. The end-groups are tentatively assigned as a lactam chain ends formed by intramolecularly assisted elimination (Scheme 1).

3.3.3 Poly(methyl methacrylate)

For PMMA-**2**-H^+ an initial mass corresponding to that expected for RAFT end-group loss occurred between 110–135 °C(see Figure 1e). For PMMA-**2** the temperature required for end-group removal temperature was slightly higher, 120–150 °C (see Figure 1f). If these mass losses correspond to end-group loss, that no concomitant unzipping is observed suggests a non-homolytic mechanism. A second mass loss is observed for PMMA-**2**-H^+ at 130-180 °C and for PMMA-**2** at 140-190 °C. These most likely correspond to unzipping. This is evidenced by the suppression of these peaks in experiments performed in the presence of DPPH.[57] However, it is not clear what initiates unzipping. The NMR of the thermolysis products show no unsaturated chain ends. These initial weight losses are followed by additional stages of polymer decomposition. These occur at temperatures typical of radical-initiated PMMA.

^{1}H NMR of kugelrohr thermolyzed samples[51] indicate complete end-group loss. SEC also confirmed complete removal of the thiocarbonylthio chromophore; the M_n decreased marginally for both PMMA-**2** and PMMA-**2**-H^+. The ^{1}H NMR did not show signals attributable to PMMA macromonomer that would be formed if end-group loss occured by a Chugaev elimination (as seen for PMMA dithiobenzoate) or would be formed by disproportionation if end-group loss occured by C-S bond homolysis (as seen for PMMA-trithiocarbonate). If end-group loss occured by C-S bond homolysis we would also expect some molecular weight increase since some radicals combine (again as seen for PMMA-trithiocarbonate). Further work is required to establish the mechanism of end-group loss and the nature of the end-groups.

PMMA-**2**-H^+ and PMMA-**2** appear unstable with respect to other RAFT-synthesized PMMA. PMMA with methyl trithiocarbonate[36] or dodecyl trithiocarbonate[56] ends shows end-group loss over the temperature range ~170-220 °C with C-S bond homolysis as the dominating mechanism. PMMA with dithiobenzoate ends ~150-220 °C[45] undergoes end-group loss by Chugaev-type elimination.

The multiple decomposition stages of PMMA formed by radical polymerization can be attributed in the trithiocarbonate thermolysis to depropagation beginning at head-to-head defects (~180 °C), depolymerization initiated from double bond defects arising from disproportionation (~280 °C) and depropagation initiated from random scission of the polymer chain (~400 °C).[36] Chong et al. found the magnitude of the lower temperature decomposition step is molar mass dependent, being larger for higher molar mass samples[36] and attributable to the greater fraction of chains possessing head to head linkages. Note that chains formed by RAFT will not possess head-to-head linkages.

The similarity in the results obtained with PMMA-**2** and PMMA-**2**-H^+ (see Figure 1e and f, Supprorting Information Figures S4 and S5) suggest that the same decomposition mechanism is responsible in each case independent of the presence of acid.

3.4 Polymers from Less Activated Monomers (LAMs)

The polymers produced from LAMs underwent end-group loss at considerably higher temperatures than those derived from MAMs. Thermolyis of protonated LAM-derived polymers were not investigated, due to the hydrolytic sensitivity of RAFT polymers with LAM-derived terminal units (e.g. poly(NVP).[58]

3.4.1 Poly(vinyl acetate)

PVAc-**1** underwent end-group mass loss between 285-325 °C (see Figure 1g), significantly higher than the MAMs in either protonated or neutral state. ^{1}H NMR spectra showed a complete removal of all signals which are attributed to the pyridine end-group and the appearance of signals in the vinylic region (~5.5 ppm) (see Figure S9) which have been previously seen in the decomposition of PVAc prepared with *S*-phthalimidomethyl *O*-ethyl xanthates.[34] In that case end-group loss was observed after heating at 220 °C and the mechanism of end-group removal for that PVAc was suggested to occur via homolysis to produce a PVAc propagating radical which might either couple and/or decay via backbiting and β-scission.[34] Evidence for this was given as an increase in the molar mass of PVAc post end-group loss and the appearance of signals attributable to head-to-head linkages and unsaturated end-groups. In contrast, of PVAc-**1** heated at 330 °C for 4 h under vacuum showed a decrease in M_n by SEC (see Supporting information Figure S8) and additional mass loss by gravimetry than calculated for the loss of the RAFT end-group alone (4 % instead of 2.5 %). The difference in behaviour may be due to the high temperature required for end-group thermolysis, which is sufficient to cause side group thermolysis. The preparative experiment suggests that thermolysis may not be a suitable process for clean end-group removal for PVAc-**1**. However, further experiments at lower temperatures are required.

The two stage mass loss observed for PVAc after loss of end-groups (Figure 1) is consistent with that reported in the literature for PVAc.[59]

3.4.2 Poly(*N*-vinylpyrrolidone)

Weight loss consistent with end-group loss for PNVP-**1** was observed between 290-315 °C; it possesses the highest onset temperature for thermally induced end-group loss of the polymers analyzed (see Figure 1j).

The thermolysis profile of PNVP-**1** post end-group loss is generally consistent with the behavior of PNVP reported in the literature [60-61] suggesting that the RAFT end-group has little or no effect on the thermal stability of PNVP. Some previous work on PNVP thermolysis[61] has indicated that a weight loss of 3-4% of total mass at 250-300 °C is associated with loss of moisture, it was important to unequivocally demonstrate loss of end-groups in our experiments. A sample of PNVP heated to 330 °C for 4 h under vacuum showed no detectable ^{1}H NMR signals attributable to the end-group pyridine functionality, the appearance of ^{1}H NMR signals in the olefinic region, and apparently intact PNVP (see Supporting Information Figure S11). This indicates that thermolysis is a suitable means of RAFT end-group removal from PNVP.

Note that the appearance of signals in the olefinic region of the ^{1}H NMR is not typical of partially thermolyzed PNVP[61] so these are likely to be associated with new unsaturated end-groups in the thermolyzed (330 °C) polymer.

4. Conclusions

The temperature of thiocarbonylthio end-group removal from the poly(MAMs) and poly(LAMs) investigated within this study were found to be strongly influenced by the identity of the monomer derived macro-R group and whether the pyridyl Z-group was in the protonated (active) or neutral (deactivated) form. MAM-based polymers bearing a protonated pyridinium chain-end underwent end-group loss via thermolysis at lower temperatures than their neutral pyridine analogues, consistent with the report of Zhou

et al. of a difference in activation energies for thermal decomposition between protonated and neutral switchable RAFT agents of approximately 40 kJ mol^{-1}.[46] Furthermore, LAM-based polymers underwent end-group thermolysis at considerably higher temperatures than MAM-based polymers. This finding is important for use of polymers prepared using these 'switchable' RAFT agents in applications demanding stability at higher temperatures.

While poly(LAMs) required a significantly higher energy input to remove the end-group than poly(MAM)-H^+ or poly(MAM), they are efficiently derivatized through heat alone. It can be concluded that thermolysis is a simple and effective method to remove the end-group of RAFT synthesized homopolymers bearing "switchable" *N*-methyl-*N*-(pyridyl dithicarbamate) end-groups.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the authors. This includes materials, synthetic details, NMR spectra and SEC chromatograms.

Appendix/Nomenclature/Abbreviations

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Keywords: thermolysis, RAFT, dithiocarbamate, end-group, polymer, thermogravimetric analysis (TGA)

References

1. Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H., Living Free-radical Polymerization by Reversible Addition-Fragmentation Chain Transfer - The RAFT Process. *Macromolecules* **1998,** *31*, 5559-62.
2. Jenkins, A. D.; Jones, R. I.; Moad, G., Terminology for reversible-deactivation radical polymerization previously called 'controlled' radical or 'living' radical polymerization. *Pure Appl. Chem.* **2010,** *82*, 483-491.
3. Moad, G.; Rizzardo, E.; Thang, S. H., Living Radical Polymerization by the RAFT Process - A Third Update. *Aust. J. Chem.* **2012,** *65* (8), 985-1076.
4. Moad, G.; Rizzardo, E.; Thang, S. H., Living Radical Polymerization by the RAFT Process - A Second Update. *Aust. J. Chem.* **2009,** *62*, 1402-1472.
5. Moad, G.; Rizzardo, E.; Thang, S. H., Living Radical Polymerization by the RAFT Process - A first Update. *Aust. J. Chem.* **2006,** *59*, 669-692.
6. Moad, G.; Rizzardo, E.; Thang, S. H., Living Radical Polymerization by the RAFT Process. *Aust. J. Chem.* **2005,** *58*, 379-410.
7. Keddie, D. J., A guide to the synthesis of block copolymers using reversible-addition fragmentation chain transfer (RAFT) polymerization. *Chem. Soc. Rev.* **2014,** *43* (2), 496-505.
8. Moad, G., RAFT Polymerization to form Stimuli-Responsive Polymers. *Polym. Chem.* **2017,** *8* (1), 177-219.
9. Keddie, D. J.; Moad, G.; Rizzardo, E.; Thang, S. H., RAFT Agent Design and Synthesis. *Macromolecules* **2012,** *45* (13), 5321-5342.
10. Benaglia, M.; Chiefari, J.; Chong, Y. K.; Moad, G.; Rizzardo, E.; Thang, S. H., Universal (Switchable) RAFT Agents. *J. Am. Chem. Soc.* **2009,** *131* (20), 6914-6915.
11. Moad, G.; Benaglia, M.; Chen, M.; Chiefari, J.; Chong, Y. K.; Keddie, D. J.; Rizzardo, E.; Thang, S. H., In Non-Conventional Functional Block Copolymers; Theato, P., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011. In *In Non-Conventional Functional Block Copolymers; Theato, P., et al.;*
ACS Symposium Series; American Chemical Society: Washington, DC, 2011., 2011.
12. Keddie, D. J.; Guerrero-Sanchez, C.; Moad, G.; Rizzardo, E.; Thang, S. H., Switchable Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization in Aqueous Solution, *N*,*N*-Dimethylacrylamide. *Macromolecules* **2011,** *44*, 6738-6745.
13. Keddie, D. J.; Guerrero-Sanchez, C.; Moad, G.; Mulder, R. J.; Rizzardo, E.; Thang, S. H., Chain Transfer Kinetics of Acid/Base Switchable *N*-Aryl-*N*-Pyridyl Dithiocarbamate RAFT Agents in Methyl Acrylate, *N*-Vinylcarbazole and Vinyl Acetate Polymerization. *Macromolecules* **2012,** *45* (10), 4205-4215.
14. Stace, S. J.; Moad, G.; Fellows, C. M.; Keddie, D. J., The effect of Z-group modification on the RAFT polymerization of N-vinylpyrrolidone controlled by "switchable" N-pyridyl-functional dithiocarbamates. *Polym. Chem.* **2015,** *6* (40), 7119-7126.
15. Dong, H.; Zhu, Y.; Li, Z.; Xu, J.; Liu, J.; Xu, S.; Wang, H.; Gao, Y.; Guo, K., Dual Switching in Both RAFT and ROP for Generation of Asymmetric $A^2A^1B^1B^2$ Type Tetrablock Quaterpolymers. *Macromolecules* **2017,** *50* (23), 9295-9306.
16. Tselepy, A.; Schiller, T. L.; Harrisson, S.; Guerrero-Sanchez, C.; Moad, G.; Keddie, D. J., Effect of Scandium Triflate on the RAFT Copolymerization of Methyl Acrylate and Vinyl Acetate Controlled by an Acid/Base "Switchable" Chain Transfer Agent. *Macromolecules* **2018,** *51* (2), 410-418.

17. Willcock, H.; O'Reilly, R. K., End group removal and modification of RAFT polymers. *Polym. Chem.* **2010,** *1*, 149-157.
18. Moad, G.; Rizzardo, E.; Thang, S. H., End-functional polymers, thiocarbonylthio group removal/transformation and reversible addition–fragmentation–chain transfer (RAFT) polymerization. *Polym. Int.* **2011,** *60* (1), 9-25.
19. Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Krstina, J.; Moad, G.; Postma, A.; Thang, S. H., Living Polymers by the Use of Trithiocarbonates as Reversible Addition−Fragmentation Chain Transfer (RAFT) Agents: ABA Triblock Copolymers by Radical Polymerization in Two Steps. *Macromolecules* **2000,** *33* (2), 243-245.
20. Moad, G.; Chong, Y. K.; Postma, A.; Rizzardo, E.; Thang, S. H., Advances in RAFT polymerization: the synthesis of polymers with defined end-groups. *Polymer* **2005,** *46* (19), 8458-8468.
21. Patton, D. L.; Mullings, M.; Fulghum, T.; Advincula, R. C., A Facile Synthesis Route to Thiol-Functionalized α,ω-Telechelic Polymers via Reversible Addition Fragmentation Chain Transfer Polymerization. *Macromolecules* **2005,** *38* (20), 8597-8602.
22. Plummer, R.; Hill, D. J. T.; Whittaker, A. K., Solution Properties of Star and Linear Poly(N-isopropylacrylamide). *Macromolecules* **2006,** *39* (24), 8379-8388.
23. Xu, J.; He, J.; Fan, D.; Wang, X.; Yang, Y., Aminolysis of Polymers with Thiocarbonylthio Termini Prepared by RAFT Polymerization: The Difference between Polystyrene and Polymethacrylates. *Macromolecules* **2006,** *39* (25), 8616-8624.
24. McCormick, C. L.; Lowe, A. B., Aqueous RAFT Polymerization: Recent Developments in Synthesis of Functional Water-Soluble (Co)polymers with Controlled Structures. *Acc. Chem. Res.* **2004,** *37* (5), 312-325.
25. Scales, C. W.; Convertine, A. J.; McCormick, C. L., Fluorescent Labeling of RAFT-Generated Poly(*N*-isopropylacrylamide) via a Facile Maleimide−Thiol Coupling Reaction. *Biomacromolecules* **2006,** *7* (5), 1389-1392.
26. Perrier, S.; Takolpuckdee, P.; Mars, C. A., Reversible addition-fragmentation chain transfer polymerization: End group modification for functionalized polymers and chain transfer agent recovery. *Macromolecules* **2005,** *38* (6), 2033-2036.
27. Chen, M.; Moad, G.; Rizzardo, E., Thiocarbonylthio end group removal from RAFT-synthesized polymers by a radical-induced process. *J. Polym. Sci., Part A: Polym. Chem.* **2009,** *47* (23), 6704-6714.
28. Chong, Y. K.; Moad, G.; Rizzardo, E.; Thang, S. H., Thiocarbonylthio End Group Removal from RAFT-Synthesized Polymers by Radical-Induced Reduction. *Macromolecules* **2007,** *40* (13), 4446-4455.
29. Tong, Y.-Y.; Dong, Y.-Q.; Du, F.-S.; Li, Z.-C., Block copolymers of poly(ethylene oxide) and poly(vinyl alcohol) synthesized by the RAFT methodology. *J. Polym. Sci., Part A: Polym. Chem.* **2009,** *47* (7), 1901-1910.
30. Chong, J. Y. T.; Keddie, D. J.; Postma, A.; Mulet, X.; Boyd, B. J.; Drummond, C. J., RAFT preparation and the aqueous self-assembly of amphiphilic poly(octadecyl acrylate)-block-poly(polyethylene glycol methyl ether acrylate) copolymers. *Colloids Surf., A* **2015,** *470*, 60-69.
31. Sykes, K. J.; Harrisson, S.; Keddie, D. J., Phosphorus-Containing Gradient (Block)Copolymers via RAFT Polymerization and Postpolymerization Modification. *Macromol. Chem. Phys.* **2016,** *217* (20), 2310-2320.
32. Li, C.; He, J.; Zhou, Y.; Gu, Y.; Yang, Y., Radical‐induced oxidation of RAFT agents−A kinetic study. *J. Polym. Sci., Part A: Polym. Chem.* **2011,** *49* (6), 1351-1360.
33. Gruendling, T.; Dietrich, M.; Barner-Kowollik, C., A Novel One-Pot Procedure for the Fast and Efficient Conversion of RAFT Polymers into Hydroxy-Functional Polymers. *Aust. J. Chem.* **2009,** *62* (8), 806-812.

34. Postma, A.; Davis, T. P.; Li, G.; Moad, G.; O'Shea, M. S., RAFT Polymerization with Phthalimidomethyl Trithiocarbonates or Xanthates. On the Origin of Bimodal Molecular Weight Distributions in Living Radical Polymerization. *Macromolecules* **2006,** *39* (16), 5307-5318.
35. Postma, A.; Davis, T. P.; Moad, G.; O'Shea, M. S., Thermolysis of RAFT-Synthesized Polymers. A Convenient Method for Trithiocarbonate Group Elimination. *Macromolecules* **2005,** *38* (13), 5371-5374.
36. Chong, B.; Moad, G.; Rizzardo, E.; Skidmore, M.; Thang, S. H., Thermolysis of RAFT-Synthesized Poly(Methyl Methacrylate). *Aust. J. Chem.* **2006,** *59* (10), 755-762.
37. Carmean, R. N.; Figg, C. A.; Scheutz, G. M.; Kubo, T.; Sumerlin, B. S., Catalyst-Free Photoinduced End-Group Removal of Thiocarbonylthio Functionality. *ACS Macro Lett.* **2017,** *6* (2), 185-189.
38. Zhang, W.; Yan, Y.; Zhu, X.; Qiu, Y.; Cheng, Z.; Zhu, J.; Zhang, Z., Chlorodithiocarbamate-Mediated RAFT Polymerization: A Novel Synthetic Method for ATRP Macroinitiators. *Macromol. React. Eng.* **2010,** *4* (3-4), 264-271.
39. Hasegawa, U.; van der Vlies, A. J., Polymeric micelles for hydrogen sulfide delivery. *MedChemComm* **2015,** *6* (2), 273-276.
40. Kulkarni, S.; Schilli, C.; Grin, B.; Muller, A. H. E.; Hoffman, A. S.; Stayton, P. S., Controlling the Aggregation of Conjugates of Streptavidin with Smart Block Copolymers Prepared via the RAFT Copolymerization Technique. *Biomacromolecules* **2006,** *7* (10), 2736-2741.
41. Radzinski, S. C.; Foster, J. C.; Matson, J. B., Synthesis of bottlebrush polymers via transfer-to and grafting-through approaches using a RAFT chain transfer agent with a ROMP-active Z-group. *Polym. Chem.* **2015,** *6* (31), 5643-5652.
42. Extended exposure (>24 h) to neat amine (ethylene diamine) was required to achieve any appreciable conversion, rendering the aminolysis method of end-group removal synthetically impractical.
43. Gupta, J.; Keddie, D. J.; Wan, C.; Haddleton, D. M.; McNally, T., Functionalisation of MWCNTs with poly(lauryl acrylate) polymerised by Cu(0)-mediated and RAFT methods. *Polym. Chem.* **2016**.
44. Patel, V. K.; Vishwakarma, N. K.; Mishra, A. K.; Biswas, C. S.; Maiti, P.; Ray, B., Synthesis of alkyne-terminated xanthate RAFT agents and their uses for the controlled radical polymerization of *N*-vinylpyrrolidone and the synthesis of its block copolymer using click chemistry. *J. Appl. Polym. Sci.* **2013,** *127* (6), 4305-4317.
45. Lima, V.; Jiang, X.; Brokken-Zijp, J.; Schoenmakers, P. J.; Klumperman, B.; Van Der Linde, R., Synthesis and characterization of telechelic polymethacrylates via RAFT polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **2005,** *43* (5), 959-973.
46. Zhou, Y.; He, J.; Li, C.; Hong, L.; Yang, Y., Dependence of Thermal Stability on Molecular Structure of RAFT/MADIX Agents: A Kinetic and Mechanistic Study. *Macromolecules* **2011,** *44*, 8446–8457.
47. Legge, T. M.; Slark, A. T.; Perrier, S., Thermal stability of reversible addition-fragmentation chain transfer/macromolecular architecture design by interchange of xanthates chain-transfer agents. *J. Polym. Sci., Part A: Polym. Chem.* **2006,** *44* (24), 6980-6987.
48. Liu, Y.; He, J.; Xu, J.; Fan, D.; Tang, W.; Yang, Y., Thermal Decomposition of Cumyl Dithiobenzoate. *Macromolecules* **2005,** *38* (24), 10332-10335.
49. Xu, J.; He, J.; Fan, D.; Tang, W.; Yang, Y., Thermal Decomposition of Dithioesters and Its Effect on RAFT Polymerization. *Macromolecules* **2006,** *39* (11), 3753-3759.
50. Nair, C. P. R.; Clouet, G.; Chaumont, P., Functionalization of PMMA by a functional "iniferter": Kinetics of polymerization of MMA using *N*,*N*'-diethyl-*N*,*N*'-bis(2-hydroxyethyl) thiuram disulfide. *J. Polym. Sci., Part A: Polym. Chem.* **1989,** *27* (6), 1795-1809.

51. Once the end-group thermolysis temperatures were deduced, preparative scale end-group transformations were undertaken using a kugelrohr apparatus under vacuum (temperatures varied from 180–280 °C). Quantitative end-group removal was confirmed by ^{1}H NMR in all cases.
52. Hornung, C. H.; Postma, A.; Saubern, S.; Chiefari, J., Sequential flow process for the controlled polymerisation and thermolysis of RAFT-synthesised polymers. *Polymer* **2014,** *55* (6), 1427-1435.
53. For PNIPAm-**1**-H^+ and PMMA-**2**-H^+ this same loss of *p*-toluenesulfonic acid during thermolysis is obscured by concurrent polymer degradation. Additionally, *p*-toluenesulfonic acid also is not observed in the ^{1}H NMR spectra of the analogous preparative thermolysis (kugelrohr) samples as it is removed during purification by precipitation.
54. The broader temperature range reported here may be due to the different temperature ramp rate and/or sample size.
55. Moad, G.; Chong, Y. K.; Rizzardo, E.; Postma, A.; Thang, S. H., Advances in RAFT Polymerization: The Synthesis of Polymers with Defined End-Groups. *Polymer* **2005,** *46*, 8458-8468.
56. Roy, S. G.; Bauri, K.; Pal, S.; Goswami, A.; Madras, G.; De, P., Synthesis, characterization and thermal degradation of dual temperature- and pH-sensitive RAFT-made copolymers of *N*,*N*-(dimethylamino)ethyl methacrylate and methyl methacrylate. *Polym. Int.* **2013,** *62* (3), 463-473.
57. In order to ensure that the end-group removal at very low temperatures was not a result of reaction induced by trace levels of residual AIBN initiator, the TGA was carried out in the presence 2,2-diphenyl-1- picrylhydrazyl (DPPH). DPPH is expected to quench any cyanoprop-2-yl radicals formed from residual AIBN efffectively stopping the chain reaction required to quantitatively remove the RAFT-derived end-groups. Degradation of the polymer was retarded under N_2, and eliminated entirely by the presence of DPPH in air. In each case the initial loss of mass consistent with the loss of the RAFT end-group was observed (see supporting information Figures S6 and S7). This suggests that the initial thermolysis of the RAFT-derived end-group is not due to trace amounts of AIBN.
58. Pound, G.; McKenzie, J. M.; Lange, R. F. M.; Klumperman, B., Polymer-protein conjugates from ω-aldehyde endfunctional poly(*N*-vinylpyrrolidone) synthesised via xanthate-mediated living radical polymerisation. *Chem. Commun.* **2008,** (27), 3193-3195.
59. McNeill, I. C.; Jamieson, A.; Tosh, D. J.; McClune, J. J., The thermal degradation of copolymers of vinyl acetate with methyl methacrylate and other monomers. *Eur. Polym. J.* **1976,** *12* (5), 305-312.
60. Peniche, C.; Zaldívar, D.; Pazos, M.; Páz, S.; Bulay, A.; Román, J. S., Study of the thermal degradation of poly(*N*-vinyl-2-pyrrolidone) by thermogravimetry–FTIR. *J. Appl. Polym. Sci.* **1993,** *50* (3), 485-493.
61. Loría-Bastarrachea, M. I.; Herrera-Kao, W.; Cauich-Rodríguez, J. V.; Cervantes-Uc, J. M.; Vázquez-Torres, H.; Ávila-Ortega, A., A TG/FTIR study on the thermal degradation of poly(vinyl pyrrolidone). *J. Therm. Anal. Calorim.* **2011,** *104* (2), 737-742.

Thermolysis is shown to be a simple and effective method for thiocarbonylthio end-group removal from polymers prepared using acid/base "switchable" dithiocarbamate RAFT agents. The onset temperature for end-group loss is strongly dependent on the identity of the monomer derived macro-R group and the charge state of the pyridyl Z group of the macro-RAFT agent.

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Effect of the Z- and macro-R-group on the thermal desulfurization of polymers synthesized with acid/base "switchable" dithiocarbamate RAFT agents